

LEAD TELLURIDE NON-MAGNETIC
BONDING RESEARCH STUDY

Third Quarterly Report
for period September 1
through November 30, 1965

Contract Number NAS5-9149

Prepared for
National Aeronautics and Space
Administration
Goddard Space Flight Center
Greenbelt, Maryland

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by
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ABSTRACT

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The purpose of this study is to define the most appropriate system and process for the reproducible fabrication of low-resistance, high strength bonds of non-magnetic electrodes to PbTe and PbTe-SnTe thermoelectric alloys. During this period, study of diffusion-bonding of W electrodes to $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$ thermoelements was continued. Experiments in bonding to dense PbTe and $\text{Pb}_{.7}\text{Sn}_{.3}\text{Te}$ with W electrodes were conducted. Reaction of W with PbTe was examined. Life testing and physical and chemical evaluation of thermoelements were continued.

I. INTRODUCTION

This program comprises an investigation of the bonding of PbTe and PbTe-SnTe thermoelements to non-magnetic electrodes, and a study of the physical and chemical factors contributing to the degradation and failure of such thermocouples during extended operation. The bonding studies are directed toward the optimization of procedures for diffusion- and braze-bonding of W and Ta electrodes to n- and p-type PbTe and PbTe-SnTe. The studies of degradation and failure are aimed at elucidating the processes involved in the long-term deterioration of thermoelement properties. By obtaining some idea of the kinetics of these processes, it should be possible to predict the long-term behavior of bonded thermoelements.

Work during this quarter was concerned with diffusion-bonding of W to $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$, PbTe and $\text{Pb}_{.7}\text{Sn}_{.3}\text{Te}$. Reaction of PbTe with W was studied briefly and investigation of other PbTe-metal reactions is discussed. Life-testing, mainly of p-type elements, and physical and chemical evaluation of thermoelements were continued.

II. BONDING STUDIES

A. P-type Diffusion Bonding to W

A group of elements was prepared by the "standard" procedure: 1800 grit lapping of element and electrode surfaces, 30 g/cm^2 pressure, 830°C for twenty minutes. These elements were virtually identical in average properties to another previously prepared lot reported in detail in the Second Quarterly Report. Over-all average contact resistance was $65 \mu\Omega$; 80 percent of the bonds were less than $100 \mu\Omega$, and the average of this group was $50 \mu\Omega$ (equivalent contact resistivity of $15 \mu\Omega\text{-cm}^2$). Measurements of the Seebeck voltage made on the elements alone, the elements assembled with electrodes, and on the bonded elements showed very little loss in output from bonding. The difference in output between the loose electrode assembly and bonded elements was less than 3 percent.

The similarity between these groups of elements is encouraging. A reasonable degree of reproducibility and control of most of the parameters of the bonding process is implied.

A series of experiments was subsequently initiated to determine the effects of variation of four process parameters: surface preparation, pressure, time, and temperature. The results of the first few runs, barring some experimental mishaps, were uniformly poor. Bond resistances were generally very high, $0.5 \text{ m}\Omega$ and higher; a number of the high resistance bonds separated easily, displaying only spotty bonding, while others came apart with some difficulty and sizeable pieces of the element remained attached to the electrode. The curious aspect of all this was that previously any bond in the area of $0.2 \text{ m}\Omega$ and up was found to be weak and bonded only at a few points. In addition, the resistance of some bonds was found to increase during room temperature measurements. This, combined with the relatively strong, high resistance bonds, pointed to the possibility of (internal) cracking. Some of the bonded elements and two new elements were sectioned. One immediately apparent feature was an unusual amount of porosity, as can be seen in Figs. 1 and 2; the second was an almost continuous series of microcracks just under the surface of the elements (see Fig. 1). These cracks resulted in the elements being virtually encased with a more-or-less adherent layer of material. When the elements were bonded, these cracks tended to grow somewhat (in some cases they either grew considerably or were already too large to be termed microcracks) as can be seen in Fig. 2. Any explanation for the existence of the excessive porosity and cracked surface in this batch of elements would be entirely speculative and basically irrelevant to the study. One question which should be investigated is whether the cracks grew as result of bonding, i. e. stresses from the electrode, or merely from thermal (cycling) stresses. This will be studied, for it has wider relevance than merely the poor performance of one lot of material.

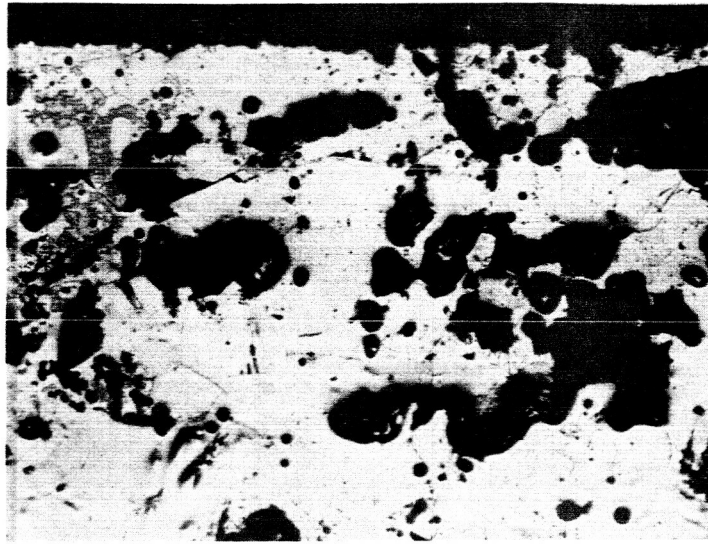


Fig. 1 Edge of unbonded p-type element showing microcracks and excessive porosity (X100).

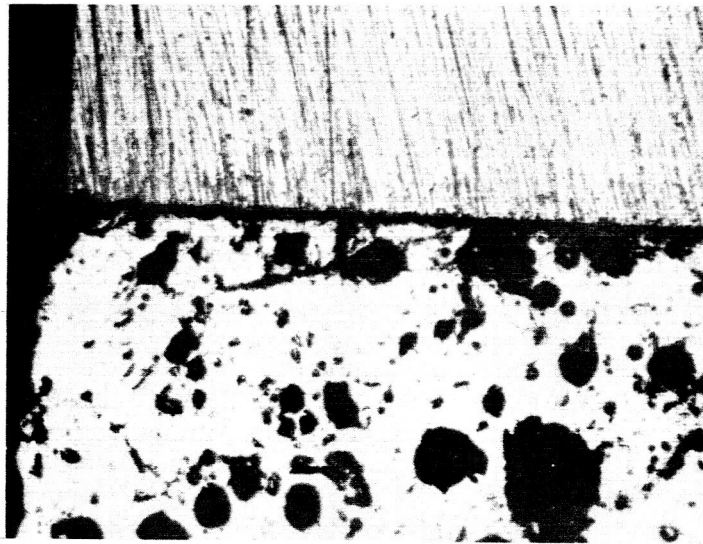


Fig. 2 Bonded p-type elements from same lot as above. Note crack at center running at a slight angle to junction. W at top (X50).

B. Diffusion Bonding of Dense PbTe

Samples of 100% dense PbTe and $\text{Pb}_{.7}\text{Sn}_{.3}\text{Te}$ prepared by an ultrasonic casting process were measured and prepared by grinding to shape and lapping the contact surfaces. The PbTe samples were doped with .03 mol % PbI_2 and the $\text{Pb}_{.7}\text{Sn}_{.3}\text{Te}$ p-type samples were undoped. Element surfaces were lapped to 1800 grit, while electrodes were 1800 or 180 grit. None of the samples, n- or p-type, bonded to the W electrodes. Temperatures to within 10° of the melting points of the alloys and times of an hour at temperature did not produce any bonding. Pressures were generally 30 g/cm^2 ; however, 200 g/cm^2 pressures showed no improvement. We are reasonably confident that the oxygen content of these materials is quite low. The same jigs were used for bonding the ultrasonic material as are normally used; there were no signs of oxidation or even of appreciable sublimation, except at very high temperatures.

To test the possibility of bonding by a vapor transport process, some experiments were made with the ultrasonically cast material in which iodine was evaporated on the contact surfaces of the elements prior to bonding. Particles of iodine and lead iodide were also placed in small holes in the element surface in other experiments. Results were inconclusive. Some spotty bonding occurred in the iodine-treated samples; however, none of the bonds was strong enough to survive measurement.

These results present some interesting problems. We know, for example, that these materials and pure PbTe and SnTe are not totally incompatible with W. All have been melted on and found to adhere very well, yet the solid materials show virtually no tendency to bond at all. The pressed and sintered PbTe and $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$ materials bond quite readily while still solid. There are three possible important differences between the materials: physical structure, deviations from stoichiometry, and dopants and impurities.

The physical structure difference consists of what might be called the "state of aggregation" of the material. The porous nature of the sintered elements could be an important factor in bonding. The ratio of

real to geometric surface area for a p-type element was found to be greater than 250. If even only a quarter of this were "effective" (the permeability of the pore structure accessible to the surface is perhaps greater to a gas under pressure, as in the BET method, than to escaping vapors) it would result in a 60 times greater "bonding activity", assuming that bonding is dependent on something like sublimation and vapor transport. The only non-stoichiometry which would seem to have any effect on bonding would be excess Te in p-type material. Lead is the only excess element possible in n-type material, and of course forms no compounds with W. The role of impurities in the bonding process is difficult to predict. The concentrations are not high, as can be seen in the analyses in Section IV. Dopants, if they were halogens or high vapor pressure metals, could be important in a vapor transport process.

The experiments suggested by these results, which would permit reasonable interpretation, are primarily with the "state of aggregation"; that is, pressing and sintering pure and ultrasonically cast PbTe and PbTe-SnTe, then attempting to bond to the resulting material; and conversely casting 3 M' s compositions to produce a dense structure.

C. Reaction of W with PbTe

Some preliminary experiments were done to investigate the nature of the W-PbTe bond. The results from the electron beam microprobe indicate no appreciable compound formation, and the results of the experiments with dense PbTe also indicate that the bond may be the result of another component.

Initially, pure PbTe and PbTe from n-type thermoelements were melted onto W electrodes at 925° for about ten minutes. Examination of these specimens indicated no visible reaction, as evidenced by the absence of third phase-particles. Subsequently, melts were made up of PbTe plus 20 and 0.5 atom % W. Melts were made in evacuated quartz ampoules by directly reacting the elements, and with previously reacted PbTe. Tungsten was in the form of small chunks and short pieces of 3 mil wire.

The melts were held at 1000°C for 68 and 53 hours, and allowed to air cool on removal from the furnace. Metallographic examination indicated that essentially no reaction had occurred. Figure 3 shows a small piece of W which still retains its original sharp corners. In Fig. 4 the out-of-focus area is a corner of a W chunk imbedded in PbTe. Some indication of a slight reaction is given by the pits, which appear in the photomicrograph as black dots at the grain boundaries. These were also found in one of the other three samples. Knop and Haraldsen⁽¹⁾ have prepared WTe_2 by reaction of the elements (in powder form) in evacuated ampoules at 700-800°C, for "several hours". In another experiment the W electrodes were broken from an n-type element and the material adhering to the electrodes was scraped off. X-ray powder patterns of this material showed only the reflexes of PbTe. This may, of course, only indicate that the amount of WTe_2 formed in the bond is very small, if indeed any is formed at all (the possibility exists that PbTe is more stable than WTe_2). Experiments such as these aimed at elucidating the nature of the diffusion bond are extremely important in understanding and potentially improving the bonding process and also in predicting long-term stability of bonded elements. The experiments described above are essentially preliminary and rather crude. To obtain the maximum of information a careful and systematic approach is necessary. The following section describes such an approach.

D. Chemical Stability of Junctions

To furnish a base for the evaluation of the long term chemical stability of the interfaces between lead-telluride and metals or lead-tin-telluride and metals (or brazes based on SnTe and metals) it is desirable to gather some basic information on the two phase equilibria in the ternary systems Pb-Te-M and Sn-Te-M. Investigations of this kind have played an important role in the study of compatibility of various metal alloys towards reactive elements, in particular, carbon, boron, and the like with respect to nuclear systems.

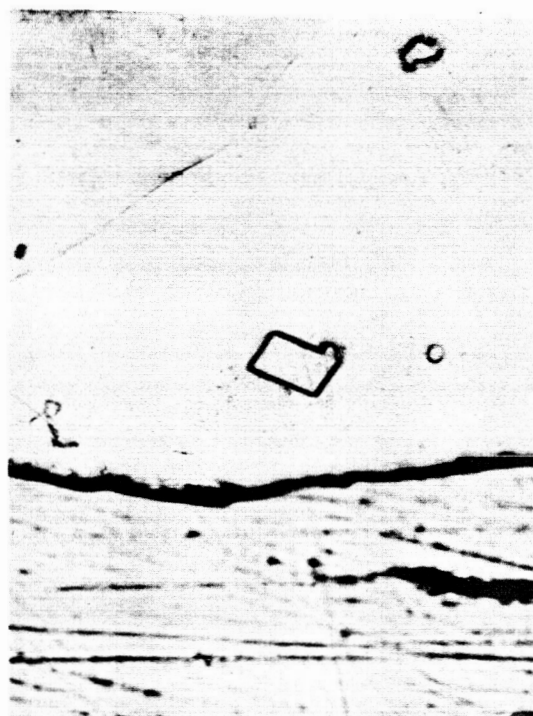


Fig. 3 Tungsten in PbTe; 1000° for 68 hours. Prepared from elements (X200).



Fig. 4 Tungsten in PbTe; 1000° for 68 hours. Prepared from PbTe and W. Possible third phase in grain boundaries (X200).

The well known "Klar-Kreuz" method of W. Guertler is the most advantageous in cases such as the ones considered here. The method is capable of giving complete compatibility information through the investigation of the constitution of (in the worst case) 6 or 7 alloys of a given ternary Pb-Te-M system. For the basis of the method consider Fig. 5. This figure shows a schematic ternary diagram containing Te and Pb (or Sn) as two components and various metals, M, as the third. On the Pb (or Sn) Te axis the compound Pb (Sn) Te is indicated. On the M-Te axis various stoichiometries of tellurides are plotted which have been obtained in metal-tellurium systems. On the M-Pb (Sn) axis no compounds are drawn, but we will discuss this axis later. What we want to establish is whether PbTe engages in stable, two-phase equilibrium with the metal at certain temperatures of interest. This is only possible if lead or tin is not in two-phase equilibrium with the M-tellurides. Everything else will violate the phase rule. We therefore anneal alloys of compositions which lie at the crosspoints of the various pseudo-binary cuts at the temperatures in question and investigate which phases form. This is done using regular phase investigation tools such as thermal analysis, metallography, and X-ray diffraction analysis. Every composition is investigated twice, once starting from prereacted PbTe and SnTe and the pure metal and once starting with the three elements involved in order to avoid kinetic effects. If Pb (Sn) Te-M is the stable equilibrium condition, in no case should any other phase but lead (tin) - telluride and the pure metal be found. The solid-solution ranges between these two can then be evaluated from the X-ray diffraction photographs and a thermal analysis would establish the eutectic temperature between them. The eutectic composition can be estimated from microsections. A section thus found to be in thermodynamic equilibrium is fully defined in its ageing properties if, in addition, the diffusion constant of the elements in each other is known.

In the cases where no two-phase equilibrium between Pb (Sn) Te and the metals is found, the situation is somewhat more complex. It is to be expected, however, that in most of these cases stable two-phase equilibria between either lead or tin itself and metal tellurides will be found

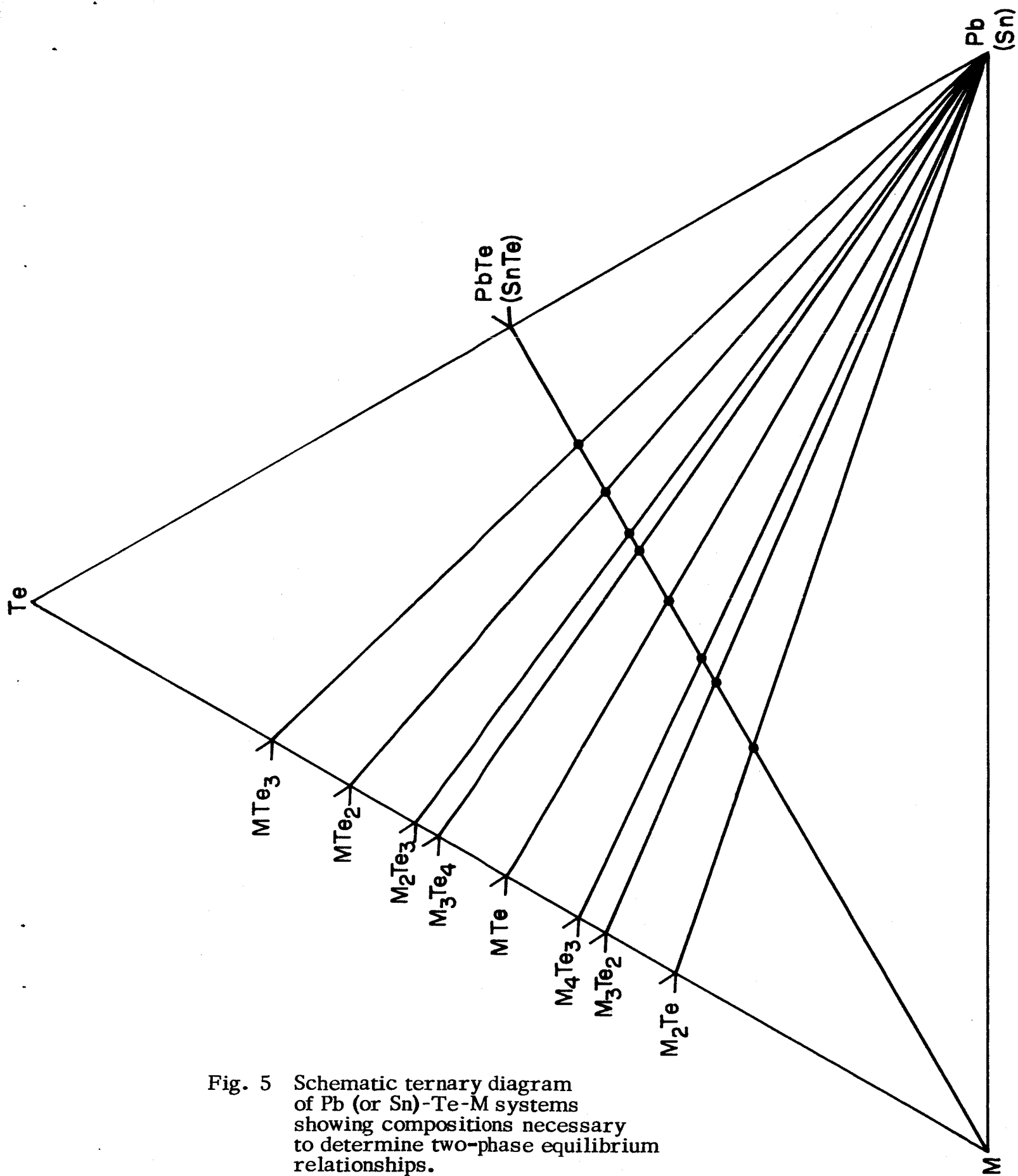


Fig. 5 Schematic ternary diagram of Pb (or Sn)-Te-M systems showing compositions necessary to determine two-phase equilibrium relationships.

(barring the existence of ternary compounds, which is unlikely), or two-phase equilibrium between the metal tellurides and compounds formed between the metals (M) and lead or tin. It seems that the former situation (equilibrium between M-telluride and metallic lead or tin) would be highly undesirable, since this would cause liquid lead or tin to be present in the junction at operating temperatures of the thermocouples, a condition likely to be disastrous in several respects, particularly during cycling. The second case is more favorable, since the intermetallic compounds formed are likely to have melting points above the operating temperature of the thermocouples. Considering metal-lead systems, it is found that no particular tendency to compound formation exists; on the contrary, many lead-metal systems contain liquid immiscibility ranges. The case of tin is more favorable, since many tin-metal compounds exist in various systems. In all cases of bonding (diffusion or braze-bonding) where the stable system is not that between Pb (Sn) Te and M, kinetic information on the reactions occurring has to be found in order to predict the behavior of the junction, just as much as the mechanical and electrical properties of the compounds formed have to be taken into account. Systematizing the phase information leads to the possibility of thermodynamic calculations and predictions about the stability of multicomponent metal alloys which are of general applicability in the context of thermoelectric generator design.

III. LIFE TESTING

A. W-Bonded P-type Elements

Two p-type SiGe-PbTe segmented elements and one W-bonded p-type element were held at 550°C for 600 hours, and two W-bonded p-type elements were held at 600°C for 570 hours. Each temperature-time group also included two electrodes with $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$ attached which had been deliberately broken from their thermoelements after bonding. All elements were in Vycor ampoules with a partial pressure of argon of about half an atmosphere at room temperature. Both bonded elements held at 600°C were intact when removed from the furnace. One electrode

was broken off in removing the element from the ampoule. The other bond was initially $60\ \mu\Omega$ and had increased to $120\ \mu\Omega$. The second element had initial contact resistances of 80 to $200\ \mu\Omega$. These measured, after testing, $500\ \mu\Omega$ and $5\text{m}\Omega$. A bond resistance of $200\ \mu\Omega$ is considered unacceptable, but it is interesting to note that this electrode was still attached to a sizeable area of $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$ when it was broken off. The fracture surfaces were oxidized, however, so the contact was largely mechanical.

Of the samples held at 550°C only one bond was carried through the removal and preparation for measurement intact. The remaining bond, a 0.1875" p-type element diffused to the W shoe of a SiGe element had an initial resistance of $35\ \mu\Omega$. The bond resistance after testing was $80\ \mu\Omega$. Thus, two out of three bonds which started with initial acceptably low resistances increased by only a factor of two. Although hardly enough to constitute a "sample", this offers some encouragement, where all p-type diffusion bonds previously tested for extended periods failed completely. These elements and some additional p-type and n-type elements have been replaced for further testing to 1000 hours or more at 600° .

As a concomitant to the life tests, tests were made on the method of protection used for life-testing. Polished W electrodes were sealed in a variety of atmosphere-ampoule combinations: vacuum-single wall ampoule, vacuum-double ampoule with evacuated outer ampoule, vacuum-double ampoule with argon-filled outer ampoule, argon-filled single ampoule, and argon filled inner-evacuated outer ampoule, and held at 600°C for 160 hours. None of the electrodes showed any trace of oxidation or discoloration.

IV. ELEMENT EVALUATION

A. Chemical Analyses

A semi-quantitative spectrographic analysis was done of n-type and p-type 3 M's thermoelements. The results are shown in Table I.

TABLE I

Semi-Quantitative Spectrographic Analysis of Thermoelements

<u>Concentration Range</u>	<u>N6</u>	<u>P7</u>
A	Pb, Te	
3B		Pb, Sn, Te
B		Mn
c	Ni	
3d	Fe	
3e		Na
e	Sn, Cu, Si	Fe, Ag, Si
3f		Ni
f	Mn, Ag, Ca	Cu, Ca, Sb, Cd
3g	Cr, Cd	Cr

Semi-Quantitative Code:

A = 10 - 100%, B = 1 - 10%, c = 0.1 - 1%, e = 0.001 - 0.01%,
f = 0.0001 - 0.001%, g = 0.00001 - 0.0001%. A number before the
letter multiplies the range. Thus 3B = 3 - 30%, 3e = 0.003 - 0.03%.

Wet chemical analyses were subsequently performed to find the Ni and Mn concentrations. These were found to be 0.043% and 1.26%, respectively. Previous analyses of p-type elements found the Mn content to be 1.10% and 0.82%. The presence of such a high concentration of Mn in p-type material is difficult to understand. Manganese is an n-type

dopant for PbTe (although this level is more than ten times the ordinary level of doping). Sodium appears in amounts (0.015 - 0.15 atom %) consistent with those used for optimum doping of PbTe p-type. The PbTe-SnTe alloys (3P) have also shown considerable excess Te in the previous analyses. This, in combination with the inherent p-type conductivity of PbTe-SnTe and the presence of Na, may be sufficient to overcome the effect of Mn. Thus, the Mn may have been added as a deoxidizer or a solid solution strengthener.

B. Pore Size Measurements

Quantitative metallographic measurements were made of pore size on photomicrographs of polished and etched sections. Measurements were made by counting the number of pores per unit area (i. e. of the photomicrograph) and the number of pores per unit length of a randomly drawn line. Fifteen lines were drawn on each photomicrograph by dropping or throwing a ruler onto the photo. Photomicrographs were made at 200 times magnification to give a 114 x 89 mm area. Three or four areas were photographed after moving the metallograph stage at random. The average radius of the pores, and the volume fraction were calculated from the measured quantities using formulae given by Rostoker and Dvorak⁽²⁾.

Measurements on two n-type elements showed volume fractions of pores to be 0.12 and 0.16 with respective average pore radii of 16 and 19 microns. Two p-type samples had volume fractions of 0.05 and 0.04 with average pore radii of 9 and 10 microns. Since density measurements have shown n-type elements to be approximately 97% dense, it seems quite possible that the high volume fraction of pores is the result of unconscious bias in selecting the areas photographed. The reverse bias may have caused the apparently low volume fraction found in the p-type samples. More carefully controlled measurements of this sort are necessary. A rough calculation using a volume fraction of 0.10 and average pore radius of 10 microns shows that the internal surface area of the pores is of the order of tens of square centimeters ($\sim 30 \text{ cm}^2$ for this case). If the ratio of real to apparent surface area found by BET measurements, $\sim 250 \text{ cm}^2/\text{cm}^2$,

is used we find an effective surface area of the pores of approximately one square meter. This serves as another indication that the majority of the oxygen found in the thermoelements is present as oxides or dissolved in the material (see Second Quarterly Report, p. 16).

C. Mechanical Testing

Measurements of tensile and compressive strengths of 3M thermoelements were made to provide a basis for mechanical testing of bonded elements. The tensile strength of essentially brittle materials may be measured by compressing a disc of the material diametrically. Tensile forces are established along the diameter between the points (lines) of contact, with the platens. The tensile stress at fracture may then be found by

$$f_t \cong \frac{2P}{\pi Dt}$$

where P is the load, D the diameter, and t the thickness of the disc.

Discs and cylinders of n and p elements of nominal dimensions 0.1875" x 0.438", 0.250" x 0.625", and 0.250" x 0.250" were tested by diametrical compression. The average value of tensile strength at fracture for n-type PbTe elements was found to be 1370 psi, and for p-type $Pb_{.5}Sn_{.5}Te$, 660 psi. The effects of different sizes did not appear to be very pronounced. N-type PbTe was ductile enough to allow some flattening of the contacts with the platens, which would tend to give higher fracture strengths than would be found by a normal tensile test, but not excessively so.

Compressive fracture strengths were also measured, using only 0.250" x 0.250" cylindrical elements. Average maximum fracture strength for n-type PbTe was 12,700 psi with a total deformation of 12%, while p-type elements had an average strength of 12,550 psi with 2.5% deformation. These results are in good agreement with measurements made previously (under Contract Nobs-86015 Bureau of Ships, Department of the Navy): p-type, 11,550 psi at 3%; n-type 14,500 at 13%. The values

published by the manufacturer are in general agreement with our findings. Tensile strengths are given as > 1000 psi and ~ 500 psi for n- and p-type, respectively. Compressive strength is given as $> 10,000$ psi.

These results give an indication of why the p-type elements cracked with the SnTe braze, as discussed in the Second Quarterly Report. As a rough approximation, the maximum shear stress is equal to one half the maximum tensile stress (this is the approximate result of most yielding criteria for ductile materials). Accordingly, the shear strengths of n and p material may be considered to be roughly 600 and 300 psi, respectively. This also gives an approximate value for the shear stress caused by expansion mismatching. Ta brazed to n-type material does not cause cracking; thus the stress is less than 600 psi, but greater than the 300 psi maximum stress capacity of p-type material.

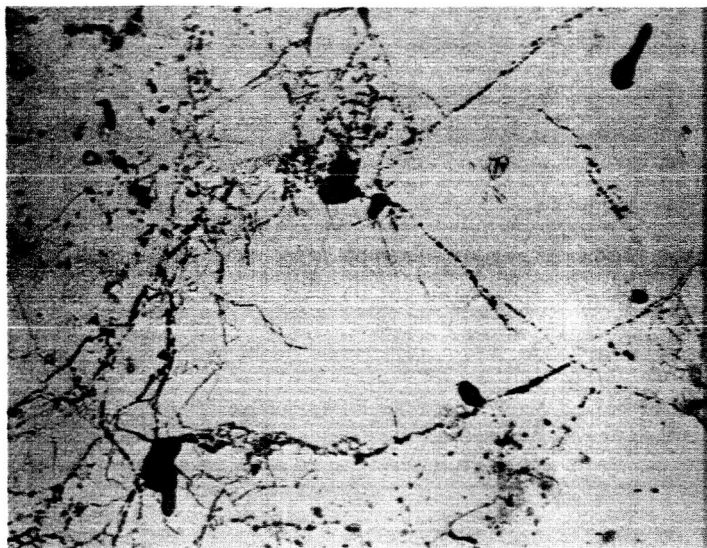
D. Asarco PbTe

The previous quarterly report presented some information on PbTe alloys manufactured by Asarco Intermetallics, Inc. Photomicrographs are shown here in Figs. 6 and 7. Considerable porosity and discontinuous grain growth similar to the 3M's materials are evident in both n- and p-type. Second phase particles of, presumably, excess constituents are present in both materials, but are particularly obvious in the n-type material at low and high magnifications.

V. CONCLUSIONS

The major effort during this quarter was directed toward further evaluation of the bonding of $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$ to W, and to experiments concerning the nature of the diffusion bond with W. The following conclusions may be made from these studies:

1. Diffusion-bonding of W to p-type $\text{Pb}_{.5}\text{Sn}_{.5}\text{Te}$ using essentially the same process as for n-type PbTe is workable and reproducible. Strict prior control of the quality of the thermoelements is necessary however.



a

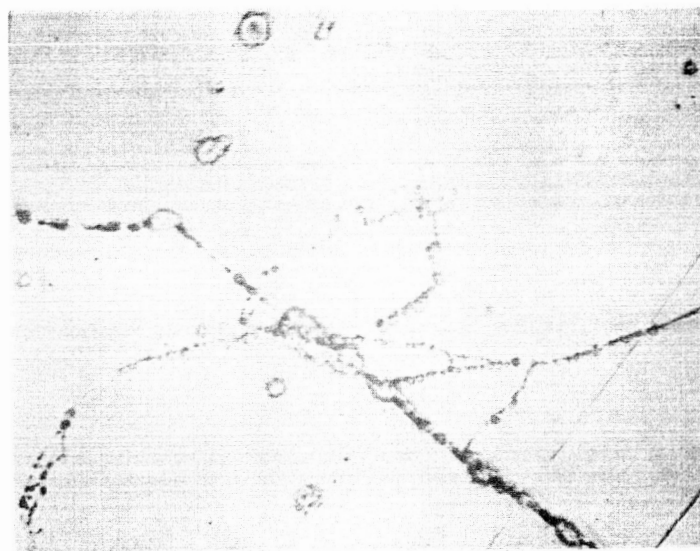


b

Fig. 6 a -- Asarco n-type PbTe (X100).
b -- Second phase particles in n-type PbTe (X500).
Etched in acid dichromate solution.



a



b

Fig. 7 a -- Asarco p-type PbTe (X100).
b -- Attack of second phase particles (black dots in a) and porosity in grain boundaries are evident (X500). Acid dichromate etch.

2. Bonding to W appears to depend on some factor - physical or chemical - peculiar to the thermoelements used. Dense PbTe materials do not bond readily by diffusion with W,

3. Preliminary experiments indicate no reaction, or very slight reaction, of PbTe with W at 1000°C.

4. Compressive fracture strengths of n- and p-type thermoelements are approximately equal at 12,500 psi; tensile fracture strength of n-type is ~ 1350 psi, while that of p-type is 650 psi.

VI. FUTURE WORK

In the next quarter, the major areas of study will be continued evaluation of p-type diffusion bonding and investigation of the bonding process in general, and life testing and analysis of life-tested elements.

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Chem. Abstr. 50, 16250 (1956).
2. W. Rostoker and J.R. Dvorak, "Interpretation of Metallographic Structures", New York: Academic Press (1965), p. 204.